

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Purification of Acrylonitrile

We, MONSANTO CHEMICAL COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of 1700, South Second Street, City of St. Louis, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to purification of monomeric acrylonitrile and more specifically to a method of removing small proportions of hydrogen cyanide present as an impurity in crude acrylonitrile.

Crude acrylonitrile as now produced may contain minor proportions up to several per cent. of hydrogen cyanide. The hydrogen cyanide present as an impurity in monomeric acrylonitrile may occur either in the form of free hydrogen cyanide or, when acetaldehyde is also present, may be combined therewith as lactonitrile. These impurities are undesirable in acrylonitrile and it is therefore necessary that they be removed. The presence of hydrogen cyanide in acrylonitrile can be determined by the phenolphthalin method described by Nicholson in *The Analyst*, Volume 66, 189 (1941).

It has been found that distillation is ineffective for the removal of such minor proportions of hydrogen cyanide in free or combined form. This method is ineffective particularly when less than one per cent. of hydrogen cyanide is present in the acrylonitrile.

According to the present invention a method of purifying monomeric acrylonitrile containing as impurities minor amounts of hydrogen cyanide as such or as lactonitrile which comprises treating the acrylonitrile with from 0.0001—0.5% by weight of an alkali metal or alkaline earth metal oxide, hydroxide, carbonate or cyanide in solution or in a solid form.

As a result of the treatment, the hydrogen cyanide is transformed into a partly soluble material which may precipitate or which may be absorbed upon the basic material when the

latter is employed in solid form. It is preferred to use an oxide, hydroxide, carbonate or cyanide of sodium, potassium, calcium or magnesium.

The process is carried out by mixing impure liquid acrylonitrile with the aqueous base such as in an extraction tower or by contacting with the solid, basic material preferably in the form of small particles. Subsequent distillation, filtration, decantation or centrifugation may be employed to remove the alkaline material together with the absorbed impurities to leave the acrylonitrile substantially free from hydrogen cyanide. The basic material may be employed in an anhydrous condition, as a solid containing water of hydration, or as an aqueous solution. The purification may also be conducted in the presence of a non-reactive solvent for the acrylonitrile, such as a hydrocarbon, for example, kerosene in which the alkaline material may be slurried or dispersed for use in the purification step.

The temperature employed is not critical, since the purification may be carried out at room temperature, or at higher temperatures, such as at the boiling point of acrylonitrile.

The invention will be illustrated in greater detail by the following examples:

EXAMPLE 1.

Monomeric acrylonitrile prepared by the reaction of hydrogen cyanide with acetylene was subjected to a preliminary distillation to obtain a crude material containing 700 parts per million of hydrogen cyanide as determined by the phenolphthalin method. This hydrogen cyanide may be present either as free hydrogen cyanide or if acetaldehyde is also present may be present as lactonitrile. The acrylonitrile was contacted with 0.125% by weight (based on the acrylonitrile) of solid sodium hydroxide in the form of pellets. The pellets were agitated in the acrylonitrile which was then filtered, leaving the unreacted sodium hydroxide plus a small quantity of a fine precipitate. It was also observed that the fine precipitate tended to be adhered upon the base. This treatment reduced the hydrogen cyanide

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content to about one part per million (0.0001%).

EXAMPLE 2.

5 Acrylonitrile monomer in crude form containing 700 parts per million of hydrogen cyanide was agitated with an equal volume of a 0.125% solution of sodium hydroxide in water. The mixture was kept at a tempera-
10 of 25° C. during the agitation step. The water layer was then withdrawn, after which the remaining material was distilled to obtain pure acrylonitrile. The purified material was found to contain less than 0.0005% of hydrogen cyanide.

EXAMPLE 3.

15 Three-hundred grams of technical grade acrylonitrile produced by the reaction of acetylene and hydrogen cyanide and containing 1000 parts per million of hydrogen cyanide were mixed with 0.3% of aqueous sodium cyanide (2.5% solution). The mixture was boiled in a distilling column operated at at total reflux for five minutes, after which
20 the solution was cooled and a trace of fine precipitate was filtered off. The filtrate was then distilled through a distilling column to yield pure acrylonitrile in 97.8% yield. The product obtained had a hydrogen cyanide content of less than 0.0005%.

EXAMPLE 4.

30 A sample of technical grade of acrylonitrile containing 881 parts per million of hydrogen cyanide was shaken with 0.5% of 10% sodium hydroxide aqueous solution. The mixture was allowed to stand at room tempera-
35 ture for 17 hours and was then assayed for hydrogen cyanide content using the phenolphthalin method. It was found that the hydrogen cyanide content was 1.7 parts per million.

40 In general it has been found that the amount of basic material which is present must be maintained within the critical concentrations of 0.0001% to 0.5% by weight relative
45 to the acrylonitrile. It is not clearly understood how the treatment operates, although it would appear that there is no direct neutralization of the hydrogen cyanide by the basic material since the proportions of the latter are
50 far less than the stoichiometric amount.

EXAMPLE 5.

55 A purification was carried out similarly to that of Example 1 but employing 0.01% of sodium carbonate dissolved in water. This aqueous solution was contacted with acrylonitrile containing about 700 parts per million of hydrogen cyanide. After agitation the aqueous phase was removed. The remaining acrylonitrile was found to have the hydrogen
60 cyanide content reduced to less than 0.0005%.

EXAMPLE 6.

A purification treatment with crude acrylo-

65 nitrile containing about 700 parts per million of hydrogen cyanide was carried out by contacting the acrylonitrile with a kerosene dispersion containing calcium hydroxide. The proportion of the calcium hydroxide corresponded to 0.001% by weight based upon the crude acrylonitrile. After the acrylonitrile and the kerosene had been mixed and then
70 separated, the hydrogen cyanide content of the acrylonitrile was less than 0.0005%.

EXAMPLE 7.

75 A purification treatment similar to that of Example 1 was carried out by the use of a dispersion of magnesium carbonate in benzene. The benzene slurry was contacted with about twice its volume of acrylonitrile so that the magnesium carbonate present corresponded to about 0.01% by weight relative to
80 the acrylonitrile. After the materials had been contacted the acrylonitrile was removed and was found to have the hydrogen cyanide content reduced to less than 0.005%.

85 The proportion of base which is employed in the treating process is critical, as explained above. However, when the basic material is employed in aqueous solution, the amount of water may be varied widely, ranging from small proportions in which the base is merely
90 slurried to larger proportions which may also accomplish other purposes, such as water-washing of the crude acrylonitrile.

What we claim is:—

95 1. A method of purifying monomeric acrylonitrile containing as impurities minor amounts of hydrogen cyanide as such or as lactonitrile which comprises treating the acrylonitrile with from 0.0001—0.5% by weight of an alkali metal or alkaline earth metal oxide, hydroxide,
100 carbonate or cyanide in solution or in a solid form.

2. A method according to Claim 1, in which the oxide, hydroxide, carbonate or cyanide is that of sodium, potassium, calcium
105 or magnesium.

3. A method according to either of the preceding claims, in which the acrylonitrile is treated with sodium hydroxide in solution or in finely divided solid form.
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4. A method of purifying monomeric acrylonitrile containing hydrogen cyanide substantially as hereinbefore described and illustrated with reference to any one of the Examples.
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5. Purified monomeric acrylonitrile whenever obtained by the process of any of the preceding claims.

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